Spectrophotometric Determination of Vanadium using Rhodamine-B in Various Environmental Samples

Summary

A new reagent system using Rhodamine-B dye for the determination of vanadium is described. The method is based on the reaction of vanadium with acidified potassium iodide to liberate iodine. The liberated iodine bleaches the pink color of Rhodamine-B, which is measured at 553 nm. Beer's law is obeyed over the concentration range of 0.08-0.64 µg ml⁻¹. The apparent molar absorptivity and Sandell's sensitivity were found to be 1.3x10³ 1 mol⁻¹ cm⁻¹ and 0.0009 µg cm⁻² respectively. The method is simple, sensitive and satisfactorily applied for the determination of vanadium in the various environmental samples at ppm levels.

Introduction

Vanadium (V) is reported to be toxic as well as an essential trace element for all living being. It is widely distributed in the earth's crust and exists in the form of different minerals and ores like carnotite, patronite, roscoelite and vanadinite (1, 2). It is also found in the phosphate rock and certain iron ores and is present in some crude oils in the form of organic complexes. Vanadium can be found in the environment in algae, plants, invertebrates, fishes and many other species. Most of the seafood contain low concentration of vanadium (<1 ng/g) as it strongly bioaccumulates, which can lead to concentrations that are found in seawater (3, 4). Some plants can accumulate vanadium up to 80 ppm in leaves and roots. Its lower concentration acts as a growth-promoting factor and participates in accumulation and fixation of nitrogen in plants (5-7).

Vanadium and its compounds are currently used as an alloying agent in the steel industry as it has good corrosion resistance to alkalis, acids and salt water. These steels are used in a variety of products, such as automobile parts, springs, ball bearings (8). About 80% of the vanadium now produced is used as ferrovanadium alloys which are invaluable in the manufacturing of jet aircraft engines, armour plates, axles, piston rods and crankshafts. Catalytic properties of vanadium containing compound is used in the manufacturing of phthalic anhydride and sulfuric acid, as well as in the production of pesticides and black dyes, inks and pigments that are used by the textile, printing and ceramic industry. It has a potential role in the production of high field magnets (~1, 75,000 gauss) super conductors, thermal or light activated resistor-conductor etc (9, 10).

In the environment it comes by the mining and milling of vanadium containing ores. Vanadium is released naturally in air through the formation of continental dust, marine aerosols and volcanic emissions. Anthropogenic sources of vanadium include the combustion of fossil fuels and residual fuel oil. Vanadium is found to be present in appreciable amount in the red mud of aluminium producing plants. The natural release
of vanadium to soils and water occurs primarily as a result of weathering of rocks and soil erosion (7, 11-13). This process usually converts less soluble trivalent form to more soluble pentavalent form, which is supposed to be more toxic. High concentration of vanadium in air occurs during the cleaning operations of oil fired boiler and heat exchangers (14). Vanadium is regarded as a potential hazardous element. The Threshold Limit Values (TLV) reported are 0.5 mg/m$^3$ of air and 0.1 mg/m$^3$ of fume. The revised IDLH (Immediately Dangerous to Life or Health) for vanadium dust is 35 mg V/m$^3$ (15, 16). Vanadium causes the inhibition of certain enzymes, which has several neurological effects. It can also cause breathing disorders, paralysis and kidney and lung damages. Workers exposed to vanadium peroxide dust were found to suffer from severe eye, nose and throat irritation. The acute effects of vanadium are cardiac and vascular disease, bleeding of liver and kidneys, inflammation of stomach and intestines, severe trembling and dizziness (17-26). Therefore, the determination of vanadium in environmental and biological samples is highly desirable.

Due to toxicity and applicability of the vanadium, various instrumental methods such as atomic absorption spectroscopy (27), electro thermal-AAS (28-30), AAS-ICPMS (31) flow-injection spectrophotometry (32), flow injection-ICP-AES (33), isotope dilution ICP-MS (34), IR spectroscopy (35), electron pair resonance spectrometry (36), thermal lens spectrophotometry (37), voltammetry (38), neutron activation analysis (39), liquid chromatography (40), gas chromatography (41), capillary electrophoresis (42) etc. have been described in the literature. Many spectrophotometric methods for the determination of vanadium based on catalytic-kinetic reaction, complex formation and solvent extraction have been reported (43, 44). Several reagents were reported for the spectrophotometric determination of vanadium such as N- arylhydroxamic acid, (45), 3-hydroxy-2-(4-methoxy phenyl)-6-methyl-4H chromen-4-one(HL)(46), 6 chlor-3-hydroxy-7-methyl-2-(2-thienyl)-4H-chromen-4-one (47), 1-8 dihydroxy naphthalene-3,6 disulfonic acid and phenyl hydrazine (48), 1-[(6-me-2-pyridal) azo]-2-hydroxy naphthalene N-oxide (49), 2,4-dihydroxyacetetophenone benzoyl hydrazone-pyridine(50), 5,7-dibromo -8-
hydroxyquinolene (51), 1,5-diphenyl carbazide (52), 4- NPH- phloroglucinol (53), pyridyl azo resorcinol (54), 5,7 dichloroxine-rhodamine 6G (55), variamine blue (56) etc. Hydroxamic acids are reported to be the most selective reagent for vanadium but are comparatively less sensitive. Here a new method for the spectrophotometric determination of vanadium is described. The method involves the liberation of iodine by the reaction of vanadium (V) with potassium iodide in acidic medium. The liberated iodine bleaches the colour of rhodamine-B. The decrease in colour is measured at 553 nm. The proposed method is simple, rapid and has been successfully applied for determination of vanadium in polluted water, soil, leaf, steel and biological samples. The results have been compared with the reported method using NPH and phloroglucinol.

**Experimental**

**Apparatus**

A Systronics spectrophotometer Model - 109 and Systronics pH meter Model-331 were used for spectral and pH measurement respectively.

**Reagents**

All chemicals used were of best available grade or the best available quality. Demineralised distilled water was used throughout the experiment.

**Standard Solution of Vanadium (Loba Chemie, Mumbai)**

To prepare stock solution of vanadium, 0.4592 g of ammonium metavanadate (Loba Chemie, Mumbai) was dissolved in lukewarm double distilled water. A few drops of conc. sulphuric acid and potassium permanganate were added drop wise with shaking till the appearance of light pink color. Volume was made up to 100 ml and vanadium was standardized using potassium permanganate (57).

**Potassium Iodide (E-Merck, Mumbai)**

A 1% (w/v) solution of potassium iodide was prepared in distilled water.
Oxalic Acid (AR)
0.1 N aqueous solution was prepared.

Rhodamine-B (BDH, Germany)
0.05 % (w/v) solution was prepared in distilled water.

Potassium Permanganate (Loba chemie, Mumbai)
0.1N aqueous solution was prepared.

Hydrochloric Acid (AR)
5M aqueous solution was prepared.

Procedure
To an aliquot of working standard containing 2-16 μg of vanadium, oxalic acid was added drop wise to destroy the excess of potassium permanganate. Then 1.0 ml hydrochloric acid was added followed by 2.0 ml of potassium iodide. The mixture was shaken gently till the appearance of yellow colour indicating the liberation of iodine. One ml of rhodamine-B was added to it and shaken for few minutes. After 15 min the volume was made upto 25 ml by adding distilled water. The decrease in absorbance of the dye was measured at 553 nm against reagent blank.

Results and Discussion

Spectral Characteristics
The absorption spectrum of rhodamine-B dye showed a maximum absorbance at 553 nm.

Effect of Reagent Concentration
Effects of varying reagent concentration were studied. It was found that 2 ml of 1% potassium iodide, 1 ml of 5 M hydrochloric acid and 1 ml of 0.05% rhodamine-B was sufficient for complete reaction.
Effect of Time and Temperature

Effect of time and temperature for the proposed reaction were also studied. It was found that liberation of iodine was more efficient at the temperature range of \(25^\circ\text{C}-35^\circ\text{C}\). Thus the reaction was carried out at room temperature.

It was noticed that at least 2 minutes were required for the liberation of iodine and 15-20 minutes time was necessary for the completion of final reaction.

Effect of pH

Constant absorbance values were obtained within the pH range of 1-2.

Sensitivity and Precision

Beer's law was obeyed over the concentration range 2-16 \(\mu\text{g}\) of vanadium per 25 ml of the final solution (0.08-0.64 \(\mu\text{g mL}^{-1}\)). The precision of the method was checked by the replicate analysis of the working standard solution containing 9 \(\mu\text{g}\) vanadium per 25 ml. The molar absorptivity, Sandell's sensitivity, detection limit, quantification limit were evaluated and are given in Table 1. Various statistical parameters were also calculated and are mentioned in Table 1.

Effect of Foreign Species

The effect of various foreign species on the reaction was studied by adding known amounts of these species to a solution containing 9 \(\mu\text{g}\) per 25 ml of vanadium. Most of the ions were found not to interfere under optimum conditions employed. The tolerance limits of foreign ions are given in Table 2.

Colour Reaction

The proposed method is based on the combination of the two well known reactions (Scheme 1), i.e.

1. Liberation of iodine with the reaction of vanadium with acidic potassium iodide.
2. Iodine forms colourless ion pair complex with rhodamine-B.
Application

The proposed method has been satisfactorily applied to the determination of vanadium in polluted water, plant materials, steel, soil and biological samples.

Determination of Vanadium in Polluted Water

Water samples were taken from different points upstream and downstream of river, which receives effluent from various industries and filtered through Whatman filter paper no. 41 and then different aliquots were analysed by the proposed and reported method (53). Recovery was also checked by preparing synthetic samples. Results are given in Table 2.

Determination of Vanadium in Soil

1 g each of soil samples, which were found to contain negligible amount of vanadium were spiked with known amounts of vanadium. These samples were fused with 5 g of sodium carbonate. After adding 25 ml of water, it was evaporated to dryness. The residue was dissolved in water, filtered and analysed by the proposed and reported method (53).

Determination of Vanadium in Steel

0.1 g amount of steel sample (No B S - 94614) containing 0.06% of vanadium was weighed accurately. It was dissolved in minimum amount of ~ 40% nitric acid. It was slowly evaporated to dryness and residue was treated with 0.5 ml of hydrochloric acid. Yellow brown precipitate of hydrated tungstic acid was obtained which was filtered off through Whatmann filter paper no 42. Filterate was again evaporated to dryness followed by addition of 0.5 ml of hydrochloric acid. Process was repeated two to three times and the contents were diluted to 25 ml. Suitable aliquots of this solution were taken and vanadium content was determined by proposed and reported method (53).
Determination of Vanadium in Plant Leaf

Dried cabbage leaf sample, each of 2 g were spiked with known amount of vanadium, digested with 0.2 g of potassium sulphate and 10 ml of Nitric acid for 30 minutes. Then 10 ml of conc. nitric acid was added and heated to dryness. For complete oxidation of leaves, the process was repeated 2 to 3 times. Residue was digested on a water bath for 30 min after adding 25 ml of 1:3 dil nitric acid to hydrolyse phosphate to orthophosphate. The contents were again evaporated to dryness and residual matter was extracted with hot distilled water, which was then filtered and cooled. Vanadium was then determined by the proposed and reported method (53).

Determination of Vanadium in Blood

5 ml of deproteinised human blood samples were spiked with known quantity of vanadium. These were treated with ~5 g potassium sulphate and 5 ml of nitric acid and heated to dryness. The process was repeated 2 - 3 times. Residue was dissolved in 25 ml of 1:3 nitric acid and kept on a water bath for digestion. It was again evaporated to dryness and the residue was dissolved in distilled water, filtered, cooled and analyzed.

Determination of Vanadium in Urine

5 ml deproteinised urine samples were taken and treated as described above. Vanadium content was then determined by the proposed and reported method (53).

Conclusion

The present method for determination of vanadium is rapid, simple and sensitive. The method has been compared with other spectrophotometric method reported for vanadium and found to be in good agreement with the reported methods (Table 6). 95 -100% recovery was obtained by the proposed method and can be easily applied for the determination of vanadium in various environmental and biological samples.
Scheme 1 - Reaction of Vanadium

Step I: Liberation of Iodine

$$\text{VO}_3^- + 6\text{I}^- + 6\text{H}^+ \rightarrow \text{V} + 2\text{I}_3^- + 3\text{H}_2\text{O}$$

Iodine

Step II: Bleaching of Rhodamine B

Iodine

Rhodamine B
(Quinonoid Form)

Rhodamine B
(Benzenoid Form)
Fig 1: Absorption spectrum of rhodamine B

Fig 2: Calibration curve for the determination of Vanadium
Fig 3: Effect of reagent concentration

Amount of potassium iodide, ml [B]

Amount of rhodamine B, ml [A]
Table 1: Photometric and Statistical Parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beer's law range (µg ml⁻¹)</td>
<td>0.08-0.64</td>
</tr>
<tr>
<td>Molar absorptivity (1 mol⁻¹ cm⁻¹)</td>
<td>1.3x 10⁵</td>
</tr>
<tr>
<td>Sandell's sensitivity (µg cm⁻²)</td>
<td>0.0009</td>
</tr>
<tr>
<td>Detection limit (µg ml⁻¹)</td>
<td>0.022</td>
</tr>
<tr>
<td>Quantification limit (µg ml⁻¹)</td>
<td>0.083</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>±0.0275</td>
</tr>
<tr>
<td>Relative standard deviation</td>
<td>6.642%</td>
</tr>
<tr>
<td>Correlation coefficient</td>
<td>0.998</td>
</tr>
</tbody>
</table>

Table 2: Effect of Foreign Ions

Concentration of Vanadium = 9 µg per 25 ml.

<table>
<thead>
<tr>
<th>Foreign Ions</th>
<th>Tolerance Limit* (µg ml⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba²⁺, Zr⁴⁺, CO₃⁻, NH₄⁺</td>
<td>3050</td>
</tr>
<tr>
<td>SO₄²⁻, Mn²⁺, Ni²⁺, PO₄³⁻</td>
<td>2050</td>
</tr>
<tr>
<td>Ag⁺, Hg₂⁺</td>
<td>1000</td>
</tr>
<tr>
<td>Br⁻, Ti⁴⁺</td>
<td>700</td>
</tr>
<tr>
<td>W⁶⁺, Cr⁵⁺</td>
<td>350</td>
</tr>
<tr>
<td>Fe³⁺, Ca²⁺</td>
<td>150</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>100</td>
</tr>
</tbody>
</table>

*Amount of interferent that causes an error of ± 2% in absorbance values.
Table 3: Determination of Vanadium in Steel Sample No BS - 94614

<table>
<thead>
<tr>
<th>Sample</th>
<th>Certified Value in %</th>
<th>Vanadium Found in %</th>
<th>Present Method*</th>
<th>Reported Method(53)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. BS 94614 (0.1g)</td>
<td>0.06%</td>
<td>0.058%</td>
<td>0.057%</td>
<td>0.057%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.057%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.059%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Mean of five observations

Table 4: Determination of Vanadium in Polluted Water-

<table>
<thead>
<tr>
<th>Sample</th>
<th>V* added (µg)</th>
<th>V* found (µg)</th>
<th>Present Method</th>
<th>Recovery</th>
<th>V* found (µg)</th>
<th>Reported Method(53)</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>River water (50 ml)</td>
<td>6</td>
<td>5.98 ±0.07</td>
<td>99.7</td>
<td>5.99 ±0.04</td>
<td>99.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>7.97 ±0.04</td>
<td>99.6</td>
<td>7.93 ±0.05</td>
<td>99.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>9.92 ±0.035</td>
<td>99.2</td>
<td>9.94 ±0.065</td>
<td>99.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polluted water (100 ml)</td>
<td>-</td>
<td>2.5 ±0.02</td>
<td>-</td>
<td>2.42 ±0.05</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>7.32 ±0.035</td>
<td>96.4</td>
<td>7.38 ±0.055</td>
<td>99.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>2.36 ±0.015</td>
<td>-</td>
<td>2.37 ±0.03</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>7.29 ±0.04</td>
<td>98.6</td>
<td>7.27 ±0.062</td>
<td>98.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

V* = Vanadium
a Mean of 6 observations
b Standard deviation
c Samples were collected from different points of upstream and downstream of rivers which receives effluent from different steel industry.
Table 5: Determination of Vanadium in Leaf, Soil, Blood and Urine Samples.

<table>
<thead>
<tr>
<th>samples</th>
<th>V⁺⁺⁺⁺⁺ Added (µg)</th>
<th>Present Method</th>
<th>Recovery</th>
<th>Reported Method (53)</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V⁺⁺⁺⁺⁺ Found(µg)</td>
<td>SD²</td>
<td></td>
<td>V⁺⁺⁺⁺⁺ Found(µg)</td>
<td>SD²</td>
</tr>
<tr>
<td>Leaf (2 g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L₁</td>
<td>4</td>
<td>3.99 ±0.05</td>
<td>99.6</td>
<td>3.98 ±0.035</td>
<td>99.5</td>
</tr>
<tr>
<td>L₂</td>
<td>6</td>
<td>5.97 ±0.045</td>
<td>99.5</td>
<td>5.96 ±0.05</td>
<td>99.2</td>
</tr>
<tr>
<td>L₃</td>
<td>8</td>
<td>7.95 ±0.06</td>
<td>99.4</td>
<td>7.97 ±0.07</td>
<td>99.6</td>
</tr>
<tr>
<td>Soil (1 g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S₁</td>
<td>4</td>
<td>3.98 ±0.015</td>
<td>99.5</td>
<td>3.96 ±0.03</td>
<td>99.0</td>
</tr>
<tr>
<td>S₂</td>
<td>6</td>
<td>5.92 ±0.07</td>
<td>98.7</td>
<td>5.95 ±0.05</td>
<td>99.2</td>
</tr>
<tr>
<td>S₃</td>
<td>8</td>
<td>7.89 ±0.03</td>
<td>98.7</td>
<td>7.92 ±0.035</td>
<td>99</td>
</tr>
<tr>
<td>Urine (5 ml)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U₁</td>
<td>8</td>
<td>7.85 ±0.045</td>
<td>98.2</td>
<td>7.82 ±0.03</td>
<td>97.8</td>
</tr>
<tr>
<td>U₂</td>
<td>10</td>
<td>9.88 ±0.06</td>
<td>98.8</td>
<td>9.90 ±0.025</td>
<td>99.0</td>
</tr>
<tr>
<td>Blood (5 ml)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B₁</td>
<td>8</td>
<td>7.90 ±0.05</td>
<td>98.2</td>
<td>7.88 ±0.06</td>
<td>98.2</td>
</tr>
<tr>
<td>B₂</td>
<td>10</td>
<td>9.88 ±0.06</td>
<td>98.8</td>
<td>9.85 ±0.05</td>
<td>98.5</td>
</tr>
</tbody>
</table>

V⁺⁺⁺⁺⁺ = Vanadium
a Mean of six observations
b Standard deviation
Table 6: Comparison with Others Spectrophotometric Method.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Reagent</th>
<th>Medium pH</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Range (µg ml$^{-1}$)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>N-Phenylbenzohydroxamic acid(54)</td>
<td>5-9 M HCl</td>
<td>510</td>
<td>2.4-7.8</td>
<td>Strong interference of various ions</td>
</tr>
<tr>
<td>2.</td>
<td>N-Phenyl cinnamohydroxamic Acid(54)</td>
<td>2.7-7.5 HCl</td>
<td>540</td>
<td>1.6-7.2</td>
<td>$\text{Tl}^{IV}$, $\text{Mo}^{VI}$, interfere</td>
</tr>
<tr>
<td>3.</td>
<td>Benzohydroxamic Acid(54)</td>
<td>1.2-5.5 HCl</td>
<td>450</td>
<td>2.8-8.2</td>
<td>$\text{Fe}^{II}$, $\text{Mn}^{II}$, $\text{Al}^{III}$ interfere</td>
</tr>
<tr>
<td>4.</td>
<td>8 Hydroxylquinolene(58)</td>
<td>0.7 M HCl</td>
<td>430</td>
<td>1.0-5.00</td>
<td>Extractive, $\text{Mo}^{VI}$, $\text{Sn}^{II}$ interfere</td>
</tr>
<tr>
<td>5.</td>
<td>3-Hydroxy-2-(4-) methoxyphenyl-6-mc-4H-chromen-4-one(46)</td>
<td>0.12 CH$_3$COOH</td>
<td>400</td>
<td>0.23-2.45</td>
<td>Extractive, $\text{Mo}^{VI}$, $\text{Sn}^{II}$ interfere</td>
</tr>
<tr>
<td>6.</td>
<td>NPH and Phloroglucinol(53)</td>
<td>12.0-12.5 NaOH</td>
<td>440</td>
<td>0.20-2.00</td>
<td>Less sensitive</td>
</tr>
<tr>
<td>7.</td>
<td>Variamine blue(56)</td>
<td>pH -3 Acetate buffer</td>
<td>570</td>
<td>0.1-2.0</td>
<td>Less sensitive, less stable dye.</td>
</tr>
<tr>
<td>8.</td>
<td>Rhodamine B Present method</td>
<td>5M HCl</td>
<td>553</td>
<td>0.8-0.64</td>
<td>More sensitive, rapid, simple, less interference</td>
</tr>
</tbody>
</table>
References

16. Izmerow, N. F., Santsky, I. V. and Sidoorv, K. K., "Toxicometric Parameters of Industrial Toxic Chemicals under Exposure" Moscow, Russia Centre of
International Projects, GNKT, 1982, p 119


